

An Investigation of Some Deriva-
tives of Orthosulphobenzoic
Acid

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE
JOHNS HOPKINS UNIVERSITY FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

—BY—

MICHAEL DRUCK SOHON

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ACKNOWLEDGMENT.

To Professor Ira Remsen, at the suggestion of whom this work was undertaken, and under the supervision of whom it was executed, the author desires to extend his acknowledgment and thanks for advice and assistance in its prosecution.

BALTIMORE, May 1896.

AN INVESTIGATION OF SOME DERIVATIVES OF ORTHOSULPHOBENZOIC ACID.

The investigations, in this laboratory, of the derivatives of orthosulphobenzoic acid, derived from the two isomeric chlorides of this acid, has shown many analogies and not less striking differences to the behavior of phthalic acid derivatives under similar conditions. It became, therefore, of interest to ascertain how the anhydride of orthosulphobenzoic acid would conduct itself toward reagents. To investigate this the present work was undertaken at the suggestion of Professor Remsen.

The anhydride of orthosulphobenzoic acid was prepared by Fahlberg and Barge,¹ by the action of acetyl chloride on the free acid; also by action of phosphorus pentachloride on the neutral potassium salt, the reaction being effected in a sealed tube, at 170°. They described it as monoclinic in crystallization, melting at 119°.

About the same time Remsen and Dohme² obtained it by heating a mixture of the acid and phosphorus pentoxide at 130°, as a sublimate consisting of fine needles, melting at 128°.

Oscar Weber,³ by the action of acetyl chloride, on metasulphoparatoluic acid, derived from "methyl saccharin," obtained its anhydride, and studied the action of ammonia upon it.

The anhydrides of various nitrosulphobenzoic acids have been obtained by workers in this laboratory.

The material used for the preparation of the anhydride in this work was the acid potassium salt of orthosulphobenzoic acid, obtained from commercial "saccharin" (containing about sixty per cent. benzoic sulphinide) by substantially the same method as described by Remsen and Saunders.⁴

The difficulties of handling and preserving the solutions in anhydrous ether or benzene led to the rejection of the methods of Fahlberg and of Weber. Sublimation did not yield the anhydride in sufficient quantity, moreover the crystals thus

¹ Ber. d. chem. Ges., **22**, 754.

² Am. Chem. J., **11**, 334.

³ Ber. d. chem. Ges., **22**, 1739.

⁴ Am. Chem. J., **17**, 347.

obtained, fine needles, decomposed much more rapidly than the large crystals obtained by the following

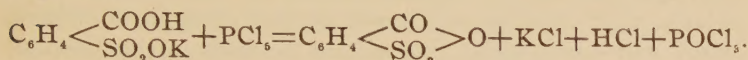
METHOD.

The well-dried and powdered acid potassium salt, (about 25 grams) is intimately mixed in a mortar, with the equivalent amount of phosphorus pentachloride, (22 grams). The temperature at which the action begins varies with the purity of the chemicals. With pure, dry reagents it is difficult to induce action, but the presence of small amounts of phosphorus oxychloride considerably lowers the required temperature. After the evolution of hydrochloric acid has ceased, the mass is heated for some time to expel some of the oxychlorides and melt the product which is then disintegrated on cooling, and placed in a continuous extractor and the separation effected by benzene. The supersaturated benzene solution in the extractor was allowed to cool very slowly and deposited clear colorless crystals often ten to fifteen millimeters longer diameter, practically pure.

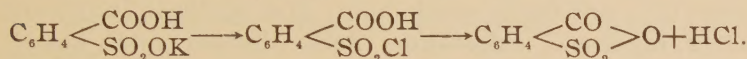
The benzene employed must be pure, or dark, sometimes blue, tarry products are obtained (an ethereal solution of the anhydride with some thiophene deposited a blue mass on exposure to the light). The presence of the phosphorus oxychloride in the solvent seems to favor the formation of better crystals.

A simple and efficient extractor was prepared from ordinary laboratory apparatus. A test tube 200 X 25 mm. was perforated with twenty or thirty pinholes made by plunging a heated platinum wire through the glass, the mouth was then contracted to about 15 mm. in diameter, and several larger openings made near this end. In this the material to be extracted was placed, suspended by a platinum wire in a long-neck balloon flask connected with inverted condenser, and immersed in a water bath, the single connection between flask and condenser was effected by means of a rubber stopper. The upper end of the condenser was provided with a calcium chloride tube.

The reaction between the salt and pentachloride may be expressed :



Limpricht and Uslar¹ have described a monochloride of the metasulphobenzoic acid. It was thought such a compound might be formed with the ortho acid and break down with the formation of the anhydride



The reaction with pentachloride was brought about at a low temperature and the resulting mass poured into cold water. A bulky flocculent precipitate separated which was washed with water until free from hydrochloric acid, and then dried between filter paper. It seemed to have a definite melting-point and gave off hydrochloric acid when heated, and the residue was the anhydride. But as the action of the pentachloride in sufficient proportion at low temperature seems to be the formation of the symmetrical dichloride. The reaction of the mass could be explained on the ground of a mixture of the anhydride and this chloride with some acid.

Remsen and Dohme, however, by the action of alcohols on the chloride prepared chlor ethers according to the reaction :



The anhydride obtained by the described method was analyzed of different samples :

- I. 0.1306 gram gave 0.2166 gram CO_2 ; 0.0300 gram H_2O .
- II. 0.1567 gram gave 0.2611 gram CO_2 ; 0.0330 gram H_2O .
- III. 0.1828 gram gave 0.3065 gram CO_2 ; 0.0389 gram H_2O .
- IV. 0.2012 gram gave 0.2543 gram BaSO_4 (Liebig).

	$\text{C}_7\text{H}_4\text{SO}_4$.	I.	II.	III.	IV.
C	45.64	45.23	45.44	45.58	
H	2.17	2.56	2.34	2.36	
S	17.39				17.39

The combustions were made with lead chromate mixture.

¹ Ann. Chem. (Liebig), 106, 30.

Analysis I. was made by Mr. E. S. Smith of this laboratory.

By the described method the anhydride is easily obtained in large clear colorless monoclinic crystals, usually showing a prism and basal plane, sometimes a small orthopinacoid. Cleavage prismatic.

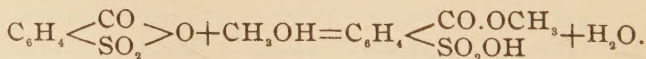
The anhydride absorbs moisture quite rapidly if powdered or in small crystals, deliquescing to a syrup of orthosulphobenzoic acid. Large whole crystals are more stable, but become dull, and finally break down. It is soluble in anhydrous ether, benzene or chloroform. Such solutions rapidly absorb moisture and deposit crystals of orthosulphobenzoic acid. The melting-point of the pure anhydride was 129.5° . It sublimes apparently at or below its melting-point and may be distilled.

The anhydride may also be prepared in quantity by distillation of the acid with phosphorus pentoxide. It did not work well with the potassium salt mixed with phosphoric acid.

ACTION WITH ALCOHOL.

Alcohols dissolve the anhydride with the formation of acid esters of orthosulphobenzoic acid. Similar esters were prepared by Remsen and Dohme by the action of alcohols on the chloride. They ascribed the general formulae given on account of the general properties and the ability to form chloroesters.

Methyl alcohol.—When the anhydride is treated with methyl alcohol (absolute or 98 per cent.) it dissolves with evolution of heat. On evaporating the alcoholic solution a thick syrup was obtained, which slowly crystallized in needles, exceedingly deliquescent and soluble; they could not be obtained in any amount.



The acid methyl ester has been described by Remsen and Dohme¹ and by Karslake.²

¹ Am. Chem. J., 9, 332.

² Dissertation J. H. U., 1895.

The *silver salt* was obtained by dissolving silver carbonate in the solution of the acid methyl ester. It crystallized from concentrated solution, in methyl alcohol, in plates. The solution darkening considerably on exposure.

Of the crystals: 0.2005 gram gave 0.0663 gram metallic silver equivalent to 33.65 per cent. silver. The formula $C_6H_4 \begin{smallmatrix} \text{CO.OCH}_3 \\ \text{SO}_2\text{OAg} \end{smallmatrix}$ requires 33.4 per cent.

Potassium salt was similar to that described by Remsen and Dohme.

0.1480 gram gave 0.1422 gram $BaSO_4$ (Liebig method).

0.1638 gram gave 0.0563 gram K_2SO_4 .

	Calculated $C_7H_4SO_2.OC_2H_5.OK.$	Found.
S	12.59	12.51
K	15.39	15.50

Ethyl alcohol dissolves the anhydride easily, the alcoholic solution evaporating to a syrup, like the corresponding methyl compound, showing crystallization.

Potassium salt, $C_6H_4 \begin{smallmatrix} \text{CO.OC}_2\text{H}_5 \\ \text{SO}_2.OK \end{smallmatrix}$, crystallized in pearly plates and was very soluble.

0.2010 gram gave 0.0649 gram K_2SO_4 , equivalent to 14.48 per cent. K; above formula requires 14.58 per cent.

Silver salt, $C_6H_4 \begin{smallmatrix} \text{SO}_2.OAg \\ \text{CO.OC}_2\text{H}_5 \end{smallmatrix}$, crystallized in needles, deliquescent.

0.1243 gram gave 0.0395 gram silver equivalent to 31.76 per cent.

ACTION WITH PHENOLS.

By the action of phenols with the anhydride, sulphonphthaleins were obtained in pure condition without difficulty. Some of these substances, especially the resorcinol derivatives have been extensively studied in this laboratory.¹ White, acting on the free acid with phenols in presence of dehydrating agents, obtained colored products, but not in any amount

¹ Am. Chem. J., 11, 73; 17, 513, 545, 556; Diss. Blackshear, 1890; Gilpin, 1892.

or in pure condition. Under the conditions employed by him the anhydride must have been present and the failure to obtain better results can only be attributed to the temperatures employed.

The phthaleins under certain conditions decompose on being heated, generally at about 150° with evolution of hydrogen sulphide. In this work it was found necessary to keep the temperature of the melt between 130° and 135° , below this, as a rule, the operation did not progress well; above decomposition often occurred, products being formed generally darker and less soluble than the sulphonphthaleins, dissolving in alkalis with only slight colors, incomparable with those of the sulphonphthaleins. These products were not farther investigated.

The sulphonphthaleins described were all produced by the direct action of the phenol and anhydride at temperatures between 130° – 138° . The use of dehydrating agents was found to be unnecessary and objectional, the yield being decreased by loss incurred in separating the dehydrating agent.

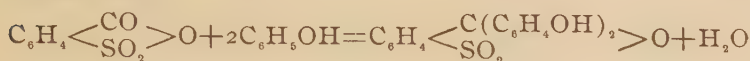
The following was the general method employed. The anhydride was mixed with somewhat more than twice the molecular equivalent of the phenol, in a porcelain crucible, and the mixture heated in an air bath at 130° – 135° for about twenty-four hours, with frequent stirring. The dark mass generally still smelled of phenol, and showed green fluorescence. The mass was disintegrated with hot water, and boiled (until free from phenol or cresol), and concentrated so that most of the sulphonphthalein crystallized out on cooling. It is then filtered and washed with water; the filtration is slow and difficult and must be aided by suction. This generally furnished the phthalein in pure condition, but often it was necessary to dissolve in alkali and reprecipitate by acids. An amorphous powder was thus obtained exceedingly difficult to filter. The loss is considerable, most of the washing being done by decantation.

An attempt was made to induce combination at lower temperatures by treating solutions of the anhydride and phenols

with dehydrating agents; only with resorcinol, however, a slight color was observed.

When the anhydride and phenol (or cresol) are mixed, a red color is seen, but the reaction does not seem to continue.

The filtrates from the sulphonphthaleins were examined but no evidence of the formation of benzoylbenzenesulphonic acids could be found. The reaction taking place may be expressed, *e. g.* :



The mother-substance sulphonphthalide was prepared by W. Jones¹ by action of hydrogen sulphide on the unsymmetrical chloride of orthosulphobenzoic acid.

The sulphonphthaleins are intensely colored substances, more soluble than the corresponding derivatives of phthalic acid, are soluble in alcohol from which they are precipitated crystalline by ether.

Varying the proportions in the melt did not alter the product, but only the rate of action and yield.



tained from the melt as a bright red crystalline powder, somewhat soluble in water, more so in alcohol, from which it was precipitated by ether as a yellowish red crystalline powder, which on removal from the liquor instantly separated ether, and solidified to a dark mass, which was apparently the same material.

The dilute alkaline solution is somewhat purer red than that of phenolphthalein; stronger alkaline solutions are purple. It is about as sensitive to alkalis and acids as phenolphthalein. The color does not disappear as readily on heating, and it might be used as an indicator with ammonia.

From the alkaline solution the sulphonphenolphthalein is precipitated as a dark red powder. By the slow cooling and evaporation of a glacial acetic acid solution, the phenolsul-

¹ Am. Chem. J., 16, 366.

phosphthalein was obtained in distinct nodules of radiating needles, blue green by reflected, and deep red by transmitted light. On analysis the following results were obtained :

- I. 0.2144 gram gave 0.5063 gram CO_2 ; 0.0876 gram H_2O .
- II. 0.1669 gram gave 0.3656 gram CO_2 ; 0.0666 gram H_2O .
- III. 0.2254 gram gave 0.1456 gram BaSO_4 .
- IV. 0.2247 gram lost 0.0028 gram at $135^\circ = 1.23$ per cent.

	$\text{C}_{19}\text{H}_{14}\text{SO}_6$.	I.	II.	III.
C	64.40	64.35	64.20	
H	3.90	4.53	4.43	
S	9.04			8.84

Phenolsulphonphthalein.—The alkaline solution of the sulphonphthalein was treated with zinc dust, the yellowish solution was filtered in an atmosphere of hydrogen, after the removal of the zinc, and most of the potassium salts, small granular crystals were formed probably of the leuco base, dihydroxytriphenylmethanesulphonic acid.

Dibromphenolsulphonphthalein, $\text{C}_{19}\text{H}_{12}\text{Br}_2\text{SO}_6$. — Phenolsulphonphthalein, in glacial acetic acid, was treated with excess of bromine dissolved in glacial acetic acid, the acid was rapidly expelled by a current of air, and the bromine derivative deposited as granular purplish crystalline powder.

0.2050 gram gave 0.0871 gram silver and 0.0983 gram BaSO_4 (Carius method), equivalent to 31.47 per cent. bromine and 6.37 per cent. sulphur. $\text{C}_{19}\text{H}_{12}\text{Br}_2\text{SO}_6$ requires 31.25 per cent. bromine and 6.27 per cent. sulphur.

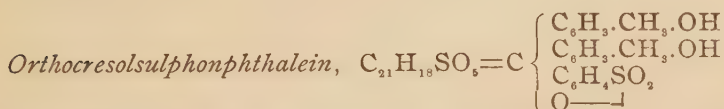
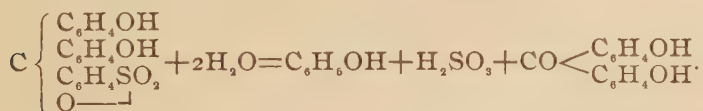
Dibromphenolsulphonphthalein gives a blue to purple color with alkalis, disappearing on standing with excess of alkali, with formation of green fluorescent solution. The acid solution is yellow. It is extremely delicate as an indicator, is sensitive to ammonia, insensitive to carbon dioxide, gives a decided blue color with *tap* water (hardness about 3°).

It was tried to secure an acetyl derivative by boiling the phenolsulphonphthalein with acetic anhydride, but apparently none was formed; anhydrous ether added to the solution separated the peculiar precipitate above mentioned, which seemed to be the same substance.

Phenolsulphonphthalein was heated in a sealed tube with concentrated hydrochloric acid for five hours at 170° to 180° , but no action could be detected. On heating for two hours at 230° to 240° decomposition was effected. Considerable pressure was observed on opening the tube; the liquid portion yielded only phenol and sulphur acids; the black solid residue yielded only a slight color to alkali, and was apparently carbon, yielding nothing on distillation.

In order to obtain a dihydroxytriphenylmethanesulphonic acid, the sulphonphthalein was boiled for fifty hours with hydrochloric acid, but no indication of such decomposition could be detected in the result. Fifty hours of boiling with excess of barium hydroxide also failed to produce any result. With dilute potassium hydroxide no action could be detected on boiling for a week; with concentrated caustic potash decomposition was effected in several hours, but the products could not be separated from the excess of alkali.

On heating the phenolsulphonphthalein in melted caustic potash the mass was found to contain sulphite, phenol, and a crystallizable substance identified as paradihydroxybenzophenone, as described by Baeyer and Burkhardt.¹



was obtained by the same method as the phenolphthalein. It crystallized from water, more easily than its lower homologue appearing beetle green by reflected and deep carmine by transmitted light. It is less soluble in water than the phenol compound, and the alkaline solutions are purple to carmine according to dilution, the neutral or dilute acid yellow, with strong acids salmon color.

On analysis the following figures were obtained:

¹ Ann. Chem., (Liebig) **202**, 196.

- I. 0.1731 gram gave 0.4182 gram CO_2 ; 0.0755 gram H_2O .
 II. 0.1558 gram gave 0.3762 gram CO_2 ; 0.0694 gram H_2O .
 III. 0.2016 gram gave 0.1240 gram BaSO_4 (Liebig method).

	$\text{C}_{21}\text{H}_{16}\text{SO}_6$.	I.	II.	III.
C	65.99	65.90	65.85	
H	4.71	4.85	4.95	
S	8.37			8.45

Dibromorthocresolsulphonphthalein, $\text{C}_{21}\text{H}_{16}\text{Br}_2\text{SO}_6$, was obtained by treating the acetic acid solution with bromine, it resembles the phenol compound in color and general properties.

On analysis :

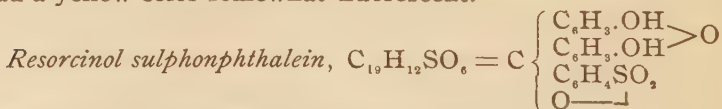
I. 0.2051 gram gave 0.0804 gram Ag and 0.0866 gram BaSO_4 .

II. 0.2280 gram gave 0.0900 gram Ag and 0.0962 gram BaSO_4 .

	$\text{C}_{21}\text{H}_{16}\text{Br}_2\text{O}_6$.	I.	II.
Br	29.26	29.10	29.05
S	5.95	5.79	5.83

On boiling the orthocresolsulphonphthalein with acetic anhydride it lost most of its color, nor did the alkaline solution show the intense color immediately. The acetyl derivative appeared to be easily saponifiable and was not isolated.

Paracresolsulphonphthalein was much more difficult to prepare than the ortho compound; it was not obtained pure. It had a yellow color somewhat fluorescent.



This substance could be produced much more easily and at lower temperature than the phenol derivatives. As shown by previous workers in this laboratory, resorcinol forms various condensation products, all intensely colored fluorescing substances. It is worthy of note, however, that while Remsen and Linn¹ and Remsen and Blackshear² produced only the di-

¹ Am. Chem. J., **11**, 73.

² Am. Chem. J., **14**, 453.

resorcinol derivative from the dioxybenzoylbenzenesulphonic acid, and McKee¹ produced the same substance from the chlorides, at low temperatures; at higher temperatures different derivatives are obtained.

In this work the materials were maintained at as low a temperature as possible to maintain action. The sulphonphthalein was obtained as a bright reddish yellow powder, intensely fluorescent in alkaline solution. The color is more red than that of fluorescein, and is more quickly destroyed by excess of alkali. The bromine derivative is not as intense in color as eosin. Sulphonfluoresceins have been described in detail by Remsen and Linn and Blackshear.

Of the phthalein:

I. 0.1358 gram gave 0.3060 gram CO_2 , and 0.0450 gram H_2O .

II. 0.2214 gram gave 0.1320 gram BaSO_4 .

	$\text{C}_{19}\text{H}_{12}\text{SO}_6$.	Found.
C	61.90	61.44
H	3.26	3.71
S	8.69	8.18

III. 0.3100 gram lost 0.0140 gram on heating at 135° for four hours, equivalent to 4.54 per cent.

IV. Dried in desiccator, over sulphuric acid, 0.2024 gram lost 0.0057 gram at 130° , equivalent to 2.81 per cent.; residue gave 0.0846 gram BaSO_4 (Liebig) equivalent to 5.73 per cent. sulphur.

V. Dried in air (eight weeks), 0.2043 gram lost 0.0094 gram at 135° , equivalent to 4.65 per cent.; residue gave 0.0868 gram BaSO_4 (Liebig) equivalent to 5.82 per cent. sulphur. The odor of hydrogen sulphide was noticeable in the air bath.

Orceinsulphonphthalein was formed easily and cleanly. It was not analyzed. It has been described in detail by Gilpin.²

Hydroquinolsulphonphthalein.—Hydroquinol reacted more slowly than resorcinol, and the mass as obtained by precipitation of the alkaline solution by acid, was a dark brown mass

¹ Dissertation J. H. U., 1895.

² *Loc. cit.*

exceedingly difficult to filter. It is less soluble than the sulphonfluorescein, the alkaline solution being brown yellow non-fluorescent.

I. 0.1930 gram gave 0.0158 gram BaSO_4 , equivalent to 8.15 per cent. sulphur.

II. 0.1544 gram gave 0.0125 gram BaSO_4 , equivalent to 8.04 per cent. sulphur.

The formula $\text{C}_{19}\text{H}_{14}\text{SO}_8$ requires 8.26 per cent. sulphur.

Pyrogallolsulphonphthalein. Sulphongallein, $\text{C}_{19}\text{H}_{10}\text{O}_8\text{S}$.—Pyrogallol reacts easily with the anhydride; the green melt was disintegrated with much hot water and purified by washing with water and obtained as a blue brown powder, somewhat soluble, giving a yellow to red color with acids, and an intense blue with alkalis, which rapidly became purple on exposure to the air, finally becoming a dirty green and brown, and depositing a brown precipitate. The addition of some stannous chloride to the alkaline solution preserves it for some time.

I. 0.2112 gram gave 0.1215 gram BaSO_4 .

II. 0.2075 gram gave 0.1185 gram BaSO_4 .

III. 0.1702 gram gave 0.3565 gram CO_2 and 0.040 gram H_2O .

	$\text{C}_{19}\text{H}_{10}\text{O}_8\text{S}$.	I.	II.	III.
C	57.28			57.12
H	2.51			2.60
S	8.14	7.89	7.84	

An attempt to prepare the phthaline was unsuccessful, decomposition resulting.

m-Amidosulphonphthalein, $\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}_4\text{S}$, was obtained as a reddish brown powder, soluble in alkalis with yellow solution, with a green fluorescence, by no means as strong as that of the sulphonfluorescein. Treatment with acetic anhydride failed to yield any derivative.

On analysis :

0.2379 gram gave 0.210 gram BaSO_4 , equivalent to 8.82 per cent. sulphur.

Formula $\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}_4\text{S}$ requires 8.74 per cent. sulphur.

p-Amidophenolsulphonphthalein isomeric with the above compound was obtained, impure, as a dark mass, more soluble than the sulphon rhodamine, gave an intense blue green with alkalies, red with acids, and is easily destroyed by oxidation in alkaline solution.

Salicylic acid melted with the anhydride yielded a bright red coloring matter.

ACTION WITH AMMONIA.

The action of ammonia on the anhydride of orthosulphobenzoic acid has been studied by Fahlberg and Barge and verified in the present work. Weber studied the action of ammonia on the anhydride of metasulphoparatoic acid, and in both cases the result was the formation of the ammonia salt of the benzamine acid.

The anhydride was dissolved in anhydrous ether (or benzene) and dry ammonia gas passed into the solution with continual shaking, until thoroughly saturated. A white crystalline precipitate was formed, this was filtered off thoroughly and washed with anhydrous ether. Nothing was obtained from the ether but a little anhydride unacted upon.

The white substance was very soluble in water from which it crystallized in nodules, and in alcohol from which it crystallized in needles, it is less soluble in absolute alcohol. It did not taste sweet, nor did it become sweet on heating, as sulphaminebenzoic acid does. In some cases a *faint* sweet taste was detected. It melted sharply at 256° – 257° .

On analysis.

I. 0.2160 gram gave 0.0274 gram N (Kjeldahl).

II. 0.2511 gram gave 0.0151 gram N (by KOH).

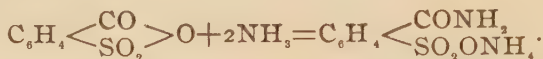
III. 0.1531 gram gave 0.1638 gram BaSO_4 .

IV. 0.1421 gram gave 0.1528 gram BaSO_4 .

V. 0.1326 gram gave 0.1388 gram BaSO_4 .

	$\text{C}_7\text{H}_9\text{SN}_2\text{O}_4$	I.	II.	III.	IV.	V.
N_2	12.88	12.67				
S	14.67			14.70	14.75	14.65
N by KOH	6.44		6.39			

Determination V. was by Mr. E. E. Reid, of this laboratory. The reaction of the anhydride and ammonia may be represented:



The result being the ammonium salt of benzaminesulphonic acid.

Barium benzaminesulphonate, $(\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{CONH}_2 \\ \text{SO}_2\end{smallmatrix}\right\rangle)_2\text{Ba}\cdot 5\text{H}_2\text{O}$, was obtained from the ammonium salt, it was very soluble in water, the solution evaporating to a thick syrup, and finally to a glass. From dilute alcohol it crystallized in white tufts of brittle needles. A similar salt is described by Karslake,¹ derived from the cyanbenzenesulphonic acid.

I. 0.4360 gram lost 0.0627 gram at 140°, and gave 0.1625 gram BaSO₄.

II. 0.3532 gram lost 0.0513 gram at 140°, and gave 0.1316 gram BaSO₄.

	(C ₆ H ₄ NSO ₂) ₂ Ba·5H ₂ O.	I.	II.
H ₂ O	14.35	14.15	14.52
Ba	21.85	22.05	21.92

Potassium benzaminesulphonate, $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{CONH}_2 \\ \text{SO}_2\text{OK}\end{smallmatrix}\right\rangle\cdot\text{H}_2\text{O}$ crystallized from dilute alcohol in small needles, easily soluble in water.

I. 0.2318 gram lost 0.0159 gram at 140° and gave 0.0784 gram K₂SO₄.

II. 0.1813 gram lost 0.0129 gram at 140° and gave 0.0633 gram K₂SO₄.

	C ₇ H ₆ SO ₄ NK·H ₂ O.	I.	II.
H ₂ O	7.00	6.88	7.11
K	15.21	15.22	15.36

The potassium salt was treated with phosphorus pentachloride, the oily chloride thus obtained was decomposed by boiling with water, neutralized by ammonia, and crystallized in

¹ Dissertation J. H. U., 1895, p. 17.

botryoidal crystals characteristic of the orthocyanbenzenesulphonic acid



The barium benzamine sulphonate was titrated with sulphuric acid, filtered and evaporated to a syrup, no crystals could be obtained. Fahlberg and Barge describe it as crystallizing in needles. Neither Jesurem¹ nor Karslake could obtain it in crystals.

ACTION WITH AROMATIC AMIDES.

With aniline and toluidines the action was analogous to that with ammonia. The anhydride and base dissolved in anhydrous benzene or ether were mixed, a pasty colorless mass separated. When equimolecular quantities were used addition of more base produced farther precipitation until a second equivalent of base had been added. The mass suspended in benzene, on long boiling usually became hard and somewhat crystalline, it was washed well with benzene and on treatment with water dissolved entirely.

By mixing the base and anhydride and heating the same substances result, but were usually darker and difficult to purify.

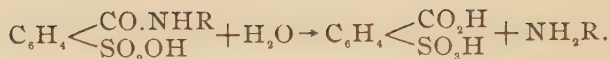
On examination these substances proved to be the salt of the base with a benzanilido acid.



The general properties of the acids are the same, the acids are very soluble, none were obtained in crystallized state, in marked distinction to the isomeric sulphanilido acids. The salts crystallize slowly from concentrated solution; often they separate as an oil, which becomes crystalline only on very long standing, and some also become liquid before dissolving.

In neutral solution they are generally stable, but often become discolored in the light. They are decomposed by long boiling with acids or strong alkali, with separation of the base, and formation of orthosulphobenzoic acid.

¹ Ber. d. chem. Ges., 26, 2288.



With phosphoruspentachloride the corresponding sulphinide derivative is formed :



These have been described by Remsen¹ and Coates and Kohler, and are decomposed on boiling with alkali, with formation of sulphanilido compounds, which are less soluble and well crystallized.

Aniline benzanilidosulphonate, $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{CO.NHC}_6\text{H}_5 \\ \text{SO}_2\text{ONHC}_6\text{H}_5\end{smallmatrix}\right\rangle$, was the only product obtained by the action of aniline on the anhydride. The mass as obtained was exceedingly soluble in water, and in alcohol, insoluble in benzene and ether. On direct evaporation of the concentration solution an oil or paste was obtained, which would not crystallize and darkened on exposure to light and air. On slow evaporation of a solution in dilute alcohol in vacuo, or better over sulphuric acid, white tufts of radiating needles were obtained. These reacted for aniline and were very soluble and difficult to crystallize. They did not lose weight on heating to 140° , but began to turn dark green.

- I. 0.2056 gram gave 0.1276 gram BaSO_4 (Carius method).
 II. 0.1851 gram gave 0.1144 gram BaSO_4 (Carius method.)
 III. 0.2621 gram gave 0.0203 gram N (Kjeldahl).

	Calculated.	I.	II.	III
S	8.64	8.52	8.49	
N	7.84			7.75

Barium benzanilidosulphonate $\left(\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{CO.NHC}_6\text{H}_5 \\ \text{SO}_2\text{O}\end{smallmatrix}\right\rangle\right)_2 \text{Ba}.$
 $5\text{H}_2\text{O}$ was very soluble in water and could not be crystallized from it. The solution evaporated to a hard transparent glass. From dilute alcohol it crystallized in fine radiating chalky

¹ Am. Chem. J., 17, 311, et seq.

needles. It is very soluble in water although the crystals dissolve but slowly.

I. 0.2211 gram lost 0.0258 gram and gave 0.0658 gram BaSO_4 .

II. 0.2131 gram lost 0.0262 gram and gave 0.0638 gram BaSO_4 .

$(\text{C}_6\text{H}_5\text{NO}_2\text{S})_2\text{Ba} \cdot 5\text{H}_2\text{O}$.		I.	II.
Ba	17.38	17.51	17.61
H_2O	11.55	11.67	11.81

Ammonium benzanilidosulphonate, $\text{C}_6\text{H}_5 \begin{matrix} \text{CONHC}_6\text{H}_5 \\ \text{SO}_2\text{ONH}_4 \cdot \text{H}_2\text{O} \end{matrix}$, is very soluble in water and crystallized quite readily in silky, radiating needles.

I. 0.2112 gram gave 0.0106 gram NH_3 .

II. 0.2326 gram lost 0.0133 gram at 130° , and gave 0.1745 gram BaSO_4 .

$\text{C}_{13}\text{H}_{14}\text{N}_2\text{SO}_4 \cdot \text{H}_2\text{O}$.		I.	II.
H_2O	5.76		5.75
S	10.25		10.27
NH_3	5.45	5.50	

Potassium benzanilidosulphonate, $\text{C}_6\text{H}_5 \begin{matrix} \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_5 \\ \text{SO}_2\text{OK} \cdot \text{H}_2\text{O} \end{matrix}$, slowly separated from dilute alcoholic solution in fine silky crystals.

I. 0.2762 gram lost 0.0165 gram at 130° , gave 0.0691 gram K_2SO_4 .

II. 0.2516 gram lost 0.0139 gram at 140° , gave 0.0651 gram K_2SO_4 .

	Calculated.	I.	II.
H_2O	6.00	5.94	5.52
K	11.73	11.22	11.50

OTHER SALTS.

The *cadmium* salt separated as a poorly crystalline powder.

I. 0.2920 gram gave 0.2015 gram BaSO_4 .

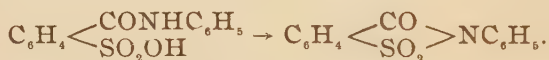
II. 0.2265 gram gave 0.0398 gram CdO .

	Calculated.	Found.
Cd	16.83	16.70
S	9.63	9.48

The *sodium*, *copper* and *lead* salts evaporated to hard glasses, and the *silver* salt decomposed on evaporation.

The *free acid* was obtained from the lead salt (by hydrogen sulphide) as a thick syrup; neither water nor alcoholic solution showed any sign of crystallization within three months.

Action of phosphorus Pentachloride.—Potassium salt was treated with phosphorus pentachloride and on adding water a white solid separated. This was washed with water and proved to be free from chlorine. It crystallized from alcohol in flat needles; on recrystallization from ether it melted sharply at 190°–191° (uncorr.). It was insoluble in acid, and in cold alkali; dissolved by boiling alkali and precipitated by acids. This, crystallized from hot water, showed melting-point 159° (uncorr.); corresponding to the anil and sulphanilido acids, the action of the pentachloride being therefore one of dehydration.



Equimolecular quantities of aniline and anhydride were heated with phosphorus pentoxide at 180°. The mass darkened considerably; and from it a substance crystallizing like the anil from alcohol and chloroform, it could not be obtained free from the product of decomposition, melting-point about 176°. By long heating with acid or more quickly by heating to 170° with hydrochloric acid, the anilido acid is converted to ortho-sulphobenzoic acid.

Paratoluidine benzparatoluidoorthosulphonate,

$\text{C}_6\text{H}_4 \begin{array}{c} \text{CO.NHC}_7\text{H}_7 \\ \text{SO}_3\text{NH}_2\text{C}_7\text{H}_7 \end{array}$, as with aniline apparently only one substance was found by action of paratoluidin. The mass as obtained was very soluble in hot water, and separated on cooling as a thick oil, which on long standing (six or eight weeks) covered by water, slowly began to crystallize, the crystals first appearing were removed from the oil to another

part of the beaker and grew in small clusters as short, sharply pointed needles.

I. 0.1530 gram gave 0.0111 gram N (Kjeldahl).

II. 0.1402 gram gave 0.0826 gram BaSO_4 .

	Calculated.	I.	II.
S	7.98		8.10
N	6.97	7.25	

Barium benztoluidosulphonate crystallized in radiate nodules, sometimes forming a crust on sides of beaker and on top of liquid. Successive crystallization indicated that it was a basic salt, and no formula could be calculated from the analyses.

I. 0.3848 gram lost 0.0260 gram at 150° and gave 0.1199 gram BaSO_4 .

II. 0.4186 gram lost 0.0280 gram at 150° and gave 0.1312 gram BaSO_4 .

	I.	II.
Ba	18.34	18.43
H_2O	6.75	6.80

Potassium salts, $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CONKC}_7\text{H}_7 \\ \diagdown \text{SO}_2\text{OK} \cdot \text{H}_2\text{O} \end{smallmatrix}$ and $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CONH} \cdot \text{C}_7\text{H}_7 \\ \diagdown \text{SO}_2\text{OK} \cdot \text{H}_2\text{O} \end{smallmatrix}$

These salts crystallized in radiating clusters and were separated by fractional precipitation of the alcoholic solution by ether. The former salt was obtained pure, the latter not.

I. 0.3233 gram lost 0.0161 gram at 140° .

II. 0.2720 gram lost 0.0134 gram at 140° and gave 0.1238 gram K_2SO_4 .

III. 0.2190 gram gave 0.0975 gram K_2SO_4 .

	$\text{C}_{14}\text{H}_{11}\text{SO}_4\text{K}_2 \cdot \text{H}_2\text{O}$.	I.	II.	III.
H_2O	4.70	4.97	4.93	
K	20.20		20.41	19.93

The free *benztoluidosulphonic acid* was obtained, by treating the barium salt with sulphuric acid, as a thick uncrystallizable mass.

Action of *phosphorus pentachloride*. The potassium salt was treated with phosphorus pentachloride, and the mass treated

with water. The resulting substance was crystallized from alcohol and identified as the paratolil described by Remsen¹ and Coates. By heating with acid at 180° the salts are converted into salts of orthosulphobenzoic acid.

Orthotoluidine benzorthotoluidoorthosulphonate.

(o) $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO.NH.C}_7\text{H}_7 \text{ (o)} \\ \diagdown \text{SO}_2.\text{ONH}_3\text{C}_7\text{H}_7 \text{ (o)} \end{smallmatrix}$ was the result of the action of the anhydride with orthotoluidine. The salt crystallized more readily than the analogous para compound, in nodules of radiating needles.

- I. 0.2455 gram gave 0.1520 gram BaSO_4 .
- II. 0.2069 gram gave 0.1235 gram BaSO_4 .
- III. 0.2233 gram gave 0.1312 gram BaSO_4 .
- IV. 0.2013 gram gave 0.0112 gram N (Kjeldahl).

	$\text{C}_{21}\text{H}_{22}\text{N}_2\text{SO}_4$.	I.	II.	III.	IV.
S	7.98	8.50	8.19	8.07	
N	6.97				6.70

Barium benztoluidosulphonate crystallized in radiating nodules. It was probably a mixture of a basic salt and the normal. No simple formula could be calculated.

Potassium benztoluidosulphonate, $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO.NHC}_7\text{H}_7 \\ \diagdown \text{SO}_3\text{K} \end{smallmatrix}$, crystallized in sharply pointed, brittle, white needles in nodules.

- I. 0.2010 gram gave 0.0538 gram K_2SO_4 .
- II. 0.3227 gram gave 0.0870 gram K_2SO_4 .
- III. 0.2607 gram gave 0.0725 gram K_2SO_4 .

	Calculated.	I.	II.	III.
K	11.88	12.01	12.09	12.49

There was also a potassium salt probably analogous to the one described under the paratoluidine derivatives, but it could not be obtained pure.

On heating the salt with acid at 180°, they are converted to salts of orthosulphobenzoic acid.

The potassium salt was treated with phosphorus pentachloride, and on treating the mass with water, a substance

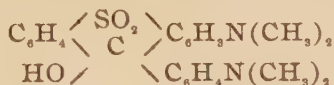
¹ *Loc. cit.*

was obtained, which on recrystallization from alcohol, melted at 170° (uncorr.) and was identified as the orthotolil described by Remsen and Coates.

Dimethylaniline.—When a benzene solution of anhydride and dimethylaniline is boiled for a long time, (four to five days) a green oil separates. A similar product is obtained by melting the anhydride with dimethylaniline, action takes place at about 90°, a green mass resulting. If the mass be heated to 180° no appreciable result takes place if the substances were mixed in equimolecular proportions. If the aniline be in excess the color disappears at 150°–160°, but the mass on being again heated with phosphorus pentoxide becomes green.

The green mass dissolves in water becomes yellow with acids and restored green by alkali. If the alkaline solution be boiled or allowed to stand it becomes bright red, apparently the complementary color. If the red solution be exactly neutralized and boiled the green color is restored. The colors are destroyed by reducing agents, *i. e.*, zinc dust, stannous chloride, etc. All attempts to separate any definite substance failed.

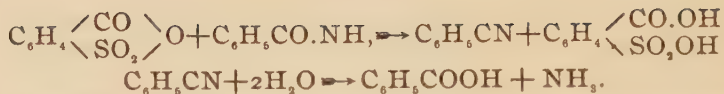
E. Fischer¹ describes *phthal green* tetramethyldiamidophenyloxanthranol made by heating phthalic anhydride with dimethyl aniline. The substance obtained resembles this, and may be an analogue of oxanthanol, *i. e.*,



ACID AMIDES.

Benzamide was boiled with the anhydride in benzene solution. Small crystals (prisms) separated, and odor of nitrile was noticed. The mass after removal of the benzene was boiled with water, and on cooling, crystals separated which were identified as benzoic acid. The solution was found to contain the acid ammonium salt of orthosulphobenzoic acid. Nothing else could be found. The action would be one of dehydration.

¹ Ann. Chem. (Liebig) 206, 107.



Acetamide acted as benzamide but with more difficulty.
 $\text{CH}_3\text{CONH}_2 \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{CN}.$

ACID ANILIDES.

Acetanilide (also *benzanilide*) and the anhydride were boiled together in benzene solution for three days. Both substances were recovered from the solution. They were also melted together for some time without any sign of action. Dehydrating agents were also employed without result.

HYDROCARBONS.

Attempts were made to obtain reaction with benzene and toluene by means of aluminum chloride and by zinc chloride, but without success.

Phosphorus pentachloride acting on the anhydride produced both chlorides of orthosulphobenzoic acid. The action was exceedingly variable, with the purity of the chemicals, temperature and time of action. With pure dry chemicals it was impossible to secure action below 120°; a small amount of oxychloride considerably lowered the temperature. At 20° no action took place even though the mass was wetted with phosphorus oxychloride.

It was concluded from numerous experiments that the formation of the *unsymmetrical chloride* was favored by high temperature, continued action and excess of pentachloride. The same results were noted in the action of the pentachloride with the potassium salts.

CONCLUSION.

In the foregoing it has been shown that the anhydride of orthosulphobenzoic acid is a well-characterized stable substance, the unsymmetrical character of the two acidifying groups being clearly indicated in the derivatives obtained.

Many of the sulphonphthaleins are readily obtained in pure

condition, and they are possessed of marked color, analogous to the phthaleins, which they resemble.

A series of sulphonic acids has been formed isomeric with the sulphamine benzoic acids from which they are distinguished by their solubility, and into which they can be converted by the successive action of phosphorus pentachloride and alkaline hydroxide.

BIOGRAPHICAL.

Michael Druck Sohon was born in Washington, D. C., December 19, 1868. His primary education was in the public schools of that city. After graduating from the High School (1887) he entered the School of Technology of the Lehigh University and was graduated (1890), receiving the degree of Analytical Chemist. He received the degree of M. S. in 1894. He was chemist at the Edgar Thomson Steel Works (Carnegie Bros. & Co., Limited) 1890-91. He subsequently worked with the late L. H. Norton, Ph. D., of the Massachusetts Institute of Technology. In the fall of 1891 he returned to the Lehigh University as instructor in chemistry, which position he occupied for three years, when he came to Johns Hopkins University (1894) where he has pursued courses in chemistry, mineralogy and physics. He was appointed University Scholar during the present year.

